

The University of Chicago

SOME REACTIONS
OF SODIUM PHENYLACETONITRILE
AND SODIUM α -PHENYL-
BUTYRONITRILE

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1933

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HELEN FISKE ALDRICH

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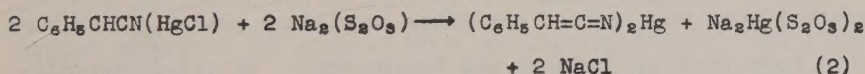


SOME REACTIONS OF SODIUM PHENYLACETONITRILE
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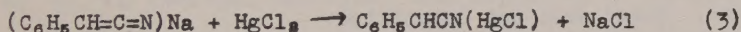
Earlier papers from this laboratory¹ have presented evidence for the existence of a tautomerism between nitride and carbide negative ions in the sodium and potassium salts of certain nitriles: $(C_6H_5-CH=C\bar{N}) \rightleftharpoons (C_6H_5-\bar{C}H-C\equiv N)$ (1)

Further evidence for the existence of these salts in a nitride form would be obtained if an N-alkylated derivative were obtained by the interaction of a nitrile salt of a heavy metal with an alkyl halide. The first step toward this goal would be the isolation in pure form of a heavy metal salt of a nitrile.

Upson, Maxwell and Parmelee² have reported the preparation of an impure silver salt of phenylacetonitrile for which they give no analytical data. This paper describes the preparation of a compound whose mercury content and behavior on ethylation make it seem likely that it is impure mercury phenylacetonitrile. It was obtained from mercuric chloride phenylacetonitrile:



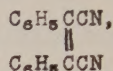
The mercuric chloride phenylacetonitrile was prepared by the action of mercuric chloride on sodium phenylacetonitrile:



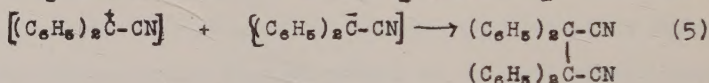
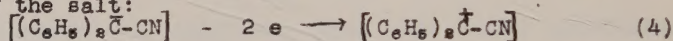
¹Rising and Zee, J. Am. Chem. Soc. 49, 541 (1927); 50, 1699 (1928); Rising, Muskat and Lowe, *ibid.*, 51, 262 (1929); Rising and Braun, *ibid.*, 52, 1069 (1930); Marberg, Doctor's Dissertation, University of Chicago (1930); Rising and Lowe, J. Am. Chem. Soc. 52, 2524 (1930); Rising and Swartz, *ibid.*, 54, 2021 (1932); Koranda, Master's Dissertation, University of Chicago (1933).

²Upson, Maxwell and Parmelee, J. Am. Chem. Soc. 52, 1971, (1930).

This paper also deals with a study of the oxidation of the sodium salts of the two nitriles, phenylacetonitrile and α -phenylbutyronitrile, separately, under certain definite conditions. The results described in the experimental part of this paper are in accord with those of previous workers who found that sodium salts of nitriles which have a hydrogen atom on the carbon atom alpha to the nitrile group react differently with iodine than salts of nitriles which have no such hydrogen atom. Thus Chalanay and Knoevenagel³ obtained cis-dicyanstilbene;



from the reaction of phenylacetonitrile with iodine in the presence of sodium ethylate. On the other hand, Auwers and Meyer,⁴ Marberg,¹ and Koranda,¹ obtained tetraphenylsuccinonitrile from sodium diphenylacetonitrile when the latter was treated with halogens. This is a reaction of the carbide tautomer. One carbide ion loses a pair of electrons before combining with another unoxidized carbide ion of the salt:



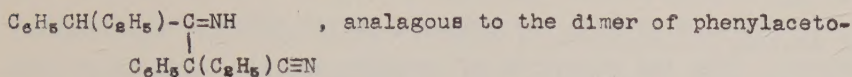
The reaction of sodium phenylacetonitrile with iodine described later was carried out under conditions somewhat different from those used by Chalanay and Knoevenagel. No cis-dicyanstilbene was isolated. The yellow amorphous powders obtained from the reaction products were found to contain nitrogen but no halogen. These were not identified.

Two products were isolated from the reaction mixture obtained when an ether solution of α -phenylbutyronitrile and iodine was treated with an alcoholic solution of sodium methylate, diphenylsuccinonitrile (compound I) and another crystalline product

³Chalanay and Knoevenagel, Ber. 25, 285 (1892).

⁴Auwers and Meyer, Ber. 22, 1227 (1889).

(compound II) of the same molecular weight and nitrogen content. Both compounds were inactive towards polarized light. Compound II gave no oxime. It was therefore not a dimer,



nitrile studied by Rising and Swartz.¹ Compounds I and II are probably stereoisomers of meso and racemic form, a phenomenon noted by Chalanay and Knoevenagel³ in the case of diphenylsuccinonitrile. That a stereochemical rather than a structural difference is involved is suggested by the fact that compound I was found to be converted to compound II by distillation and by heating in a bomb with concentrated hydrochloric acid. No means of converting compound II to compound I was discovered. All efforts to hydrolyze compound I and compound II to the corresponding dicarboxylic acids were unsuccessful.

EXPERIMENTAL PART

Volumetric method for the determination of mercury in organic compounds which contain halogens.- In view of the fact that it was necessary to carry out a number of mercury analyses it seemed advisable to develop an accurate and rapid method for the quantitative determination of mercury in organic compounds. The method described was adapted from one used by Bauer.⁵ The finely pulverized substance (0.2-0.3 g.) to be analyzed is decomposed as described by Bauer with 5 cc. of concentrated sulfuric acid⁶ and 2 to 3 cc. of 30% hydrogen peroxide. The digestion is carried out in a 500 cc. Erlenmeyer flask closed with a two-holed rubber stop-

⁵Bauer, Ber. 54, 2079 (1921).

⁶With the mercury compounds described in this paper it was found necessary to use fuming sulfuric acid to avoid the formation of a slight gray residue of unoxidized mercury.

per, one hole of which carries a 25 cc. dropping funnel, while the other carries a bent piece of glass tubing to which is attached a 20 cc. Peligot tube⁷ so constructed that 5 cc. of water fills it sufficiently to collect any escaping vapors which might contain mercury. When the digestion is complete and the contents of the flask have cooled, 150 cc. of water is added and the solution heated to boiling for ten minutes in the presence of a small piece of platinized platinum foil to aid in the decomposition of the Caro's acid formed during the digestion process. The liquid in the Peligot tube is then rinsed into the flask and the solution in the flask made alkaline to litmus with 28 per cent sodium hydroxide. Then two drops more of the sodium hydroxide are added. While the solution is still warm from the neutralization, 10 cc. of approximately 1/5 N standard solution of potassium cyanide is added from a calibrated 10 cc. burette. The amount of this potassium cyanide solution which has not reacted with mercury is determined by a Liebig titration with 1/20 N silver nitrate solution. The titer of the potassium cyanide in terms of the silver nitrate must be determined daily. If 10 cc. of potassium cyanide is found to be equivalent to (X) cc. of the silver nitrate solution, and if (Y) cc. of the silver nitrate solution is required to titrate the excess of potassium cyanide, then (X-Y) cc. of the silver nitrate is equivalent to the amount of mercury present.

$$1 \text{ cc. M/20 AgNO}_3 = 0.01003 \text{ g. Hg}$$

The method described differs from that used by Bauer in the following respects: (1) Sodium hydroxide is used to neutralize the sulfuric acid of the digestion mixture instead of ammonium hydroxide. This change was made because it was found that

⁷Houben, "Die Methoden der Organische Chemie," Georg Thieme, Leipzig, 3rd ed., 1925, p. 52.

the ammonium sulfate formed when the acid is neutralized with ammonia lowered the titer of potassium cyanide, probably due to induced hydrolysis of potassium cyanide. Sodium sulfate has no such effect. (2) The silver nitrate is standardized against mercuric chloride in the presence of that amount of sodium sulfate formed by the neutralization of 5 cc. of concentrated sulfuric acid. This precaution is necessary because although the presence of sodium sulfate has no effect on the titer of potassium cyanide by silver nitrate in the absence of mercuric ion, it has an effect when mercuric ion is present. Thus, a silver nitrate solution standardized against mercuric chloride in the presence of sodium sulfate has a lower factor value than the same silver nitrate solution standardized in the absence of sodium sulfate.

The accuracy of the method as used was established by use with organic compounds of known mercury content. With mercuric acetate the following results were obtained:

Anal. Subs., 0.1353 g., AgNO_3 (1 cc. = 0.01036 g. Hg), 8.23 cc. Calcd. for $\text{C}_4\text{H}_6\text{O}_4\text{Hg}$: Hg, 62.94%. Found: Hg, 62.99%
Mercuric benzoate was also analyzed.

Anal. Subs., 0.1113, 0.1630g., AgNO_3 (1 cc. = 0.009848 g. Hg) 5.10, 7.50 cc. Calcd. for $\text{C}_{14}\text{H}_{10}\text{O}_4\text{Hg}$: Hg, 45.31%. Found: Hg, 45.31, 45.17%.

Preparation of mercuric chloride phenylacetonitrile (Equation 3).— The sodium salt of this nitrile was prepared in an atmosphere of nitrogen as described by Braun¹ from 29.3 g. of phenylacetonitrile (b.p. 231-232°).⁸ To the filtered ethereal solution of sodium phenylacetonitrile was added 31.6 g. of mercuric chloride dissolved in 300 cc. of absolute ether. When one-half of the mercuric chloride had been added, the ether layer was bright green. A yellow brown solid was also present. As the second 15.8 g. por-

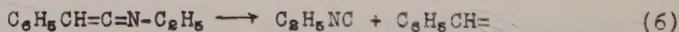
⁸ All temperatures given are uncorrected for stem exposure.

tion of mercuric chloride was added the ether layer became pale yellow, the solid colorless.

From the solid portion of the reaction products (24.5 g.) was obtained by extraction with chloroform and subsequent precipitation from the chloroform extract with a large excess of ligroin, a light yellow product (3.5 g.) which sintered at 90°, melted 105-130° and hardened again at 135-140°. It was analyzed for mercury.

Anal. Subs., 0.0610 g., AgNO_3 (1 cc. = 0.01036 g. Hg), 3.53 cc, Calcd. for $\text{C}_8\text{H}_8\text{NHgCl}$: Hg, 56.96%. Found: Hg, 56.53%.

Preparation of mercury phenylacetoneitrile.— A small amount (1 g.) of mercuric chloride phenylacetoneitrile was treated with a concentrated water solution of sodium thiosulfate, a reagent which would convert mercuric chloride phenylacetoneitrile to mercury phenylacetoneitrile (Equation 2). A few drops of acetone were added. The solid reddened immediately and the acetone-water solution became red. After the reaction mixture had stood three hours, the solid was collected on a filter, washed thoroughly with water and dried. While wet the solid was a brick red but after drying it was a brownish yellow color. It melted at 78°, but sintered below that temperature. This material, when dissolved in acetone, treated with a little ethyl iodide, and refluxed one-half hour, gave a reaction product which developed an odor of carbylamine on standing several days. This was taken as evidence that N-alkylation had occurred, the carbylamine being produced by a decomposition of the N-alkylated derivative:



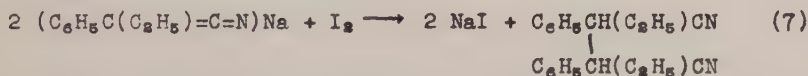
A chloroform solution of the solid which melted at 78° was poured into a large excess of low-boiling ligroin. The purified product obtained in this manner was pale yellow in color and sintered at 127°, melted at 142-150° and hardened 150-160°. It was analyzed

for mercury.

Anal. Subs., 0.0640 g., AgNO_3 (1 cc. = 0.01036 g. Hg), 2.63 cc. Calcd. for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{Hg}$: Hg, 46.36%. Found: Hg, 42.56%.

Oxidation of sodium phenylacetoneitrile with iodine.- When an ether solution which contained one mole of sodium phenylacetoneitrile was added to a solution which contained half a mole of iodine in ether, in an atmosphere of nitrogen, a series of yellow powders were obtained from the reaction products. The yellow powder obtained in the greatest quantity decomposed at 230° . It contained no halogen. Its nitrogen content was about half that of the original nitrile. No trace of cis-dicyanstilbene or of diphenylsuccinonitrile was found.

Oxidation of α -phenylbutyronitrile with iodine in the presence of sodium methylate.-



Sodium methylate, prepared from 3 g. of sodium and ten times its weight of absolute methyl alcohol, was added dropwise to a solution of 18 g. of α -phenylbutyronitrile (b.p. $115-117^\circ$ at 15 mm.), prepared by the method of Bodroux and Taboury.⁹ The apparatus used was that described by Braun, except that no provision for filtration in an atmosphere of nitrogen was needed. The ether solution gradually lost the color due to the presence of free iodine. A white crystalline precipitate of sodium iodide was deposited. The addition of the sodium methylate was continued until a negative test for free iodine was obtained. The reaction mixture was treated with water to decompose any excess sodium salt and to dissolve the precipitate of sodium iodide.

From the ether layer, dried over calcium chloride, was

⁹Bodroux and Taboury, Bull. soc. chim., ser. 4, 7, 666 (1910)

obtained a lemon yellow oil which deposited crystals. After purification by crystallization from hot alcohol these crystals melted sharply at 174° (Compound I). This crystalline material was shown by nitrogen analyses and micro-molecular weight determinations to be identical with a compound melting at 173° described by Lowe¹⁰ and identified by him as diphenyldiethylsuccinonitrile.

The lemon yellow oil from which all of the crystallized diphenyldiethylsuccinonitrile had been removed was subjected to a vacuum distillation at 4 mm. pressure. Some unchanged α -phenylbutyronitrile was recovered. At 160 - 165° there distilled 3 g. of a pale yellow, very viscous oil which solidified on standing to pure white crystals (Compound II). The later fractions consisted of a dark-colored oil which failed to crystallize and considerable resin. Compound II was found to decompose to a pasty solid at 113° and to melt over a range as the temperature of the bath was raised. It was completely melted at about 160° . A sodium fusion showed that this material contained nitrogen but no halogen. It was more soluble in alcohol and glacial acetic acid than was compound I. Nitrogen analyses by the Pregl micro-combustion method and micro-molecular weight determinations in camphor gave the following results:

Anal. Subs., 3.750, 1.902 mg., N_2 , 0.326, 0.164 cc., (26° , 24° , 742.3, 749.4 mm.) Calcd. for $C_{20}H_{20}N_2$: N, 9.72%. Found: N, 9.70, 9.77%. 0.0097 g. of subs. in 0.1178 g. of camphor lowered the melting point of camphor 11.2° . Calcd. for $C_{20}H_{20}N_2$: mol. wt. 288. Found: mol. wt. 294.

No oxime could be obtained from Compound II.

Both compound I and compound II were found to be inactive towards polarized light. The possibilities of converting one com-

¹⁰Lowe, Doctor's Dissertation, University of Chicago, (1930).

pound to the other were studied: (a) Distillation of compound I at 4 mm. pressure changed it to compound II. (b) Boiling compound I (m.p. 174°) with glacial acetic acid did not change its melting point. (c) Compound I was changed to compound II by heating in a bomb tube with concentrated hydrochloric acid for eight hours at 120°. (d) No means of converting compound II to compound I were discovered.

All attempts to hydrolyze compounds I and II failed to produce more than traces of acid products.

SUMMARY

1. Mercuric chloride phenylacetonitrile has been prepared by the action of mercuric chloride on sodium phenylacetonitrile.
2. Treatment of mercuric chloride phenylacetonitrile with sodium thiosulfate has been found to produce a compound whose mercury content and behavior make it likely that it is impure mercury phenylacetonitrile.
3. A volumetric method for the determination of mercury in organic compounds which contain halogens has been developed.
4. The action of iodine on an ether solution of sodium phenylacetonitrile has been found to produce yellow amorphous powders which contain nitrogen but no halogen.
5. The action of iodine on α -phenylbutyronitrile in the presence of sodium methylate gives diphenyldiethylsuccinonitrile and a second compound of the same molecular weight and nitrogen content as diphenyldiethylsuccinonitrile and probably stereoisomeric with it.

